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Fe (III) speciation in the high nutrient, low chlorophyll Pacific region of the Southern Ocean

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Abstract

Fe speciation was measured with competitive ligand equilibration adsorptive cathodic stripping voltammetry [Gledhill, M., Van den Berg, C.M.G., 1994. Determination of complexation of iron (III) with natural organic complexing ligands in sea water using cathodic stripping voltammetry. Mar. Chem., 47, 41–54.] in the Pacific part of the Southern Ocean between 58° and 68°30′S along the 90°W meridian. The conditional stability constant (K' with respect to $[Fe^{3+}]$) was between $10^{20.6}$ and $10^{21.6}$ when one organic ligand was detected. The ligand concentration ($[L_t]$) varied between 2.2 and 12.3 equivalents of nM Fe (nEq of Fe). The ligand concentration was at least 6 times, and generally more than 10 times, that of the total dissolvable Fe concentration. At one station a depth profile was sampled where below 200 m depth, two organic ligands were measured with $K'_1 = 10^{21}$ and $K'_2 = 10^{22.4}$. Organic complexation of Fe was similar to results found elsewhere [(Gledhill, M., Van den Berg, C.M.G., 1994. Determination of complexation of iron (III) with natural organic complexing ligands in sea water using cathodic stripping voltammetry. Mar. Chem., 47, 41–54.); (Van den Berg, C.M.G., 1995. Evidence for organic complexation in seawater. Mar. Chem., 50, 139–159.); (Rue, E.L., Bruland, K.W., 1995. Complexation of iron (III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. Mar. Chem., 50, 117–138.); (Rue, E.L., Bruland, K.W., 1997. The role of organic complexation on ambient iron chemistry in the equatorial Pacific Ocean and the response of a mesoscale iron addition experiment. Limnol. Oceanogr., 42, 901–910.)] judging from the overall organic alpha value ($K' * [L_t]$) $10^{12.4}$–$10^{13.9}$. The lower values of organic alpha were within one order of magnitude of our choice of the inorganic alpha ($10^{11.9}$, [Millero, F.J., Yao, W., Aicher, J., 1995. The speciation of Fe (II) and Fe (III) in natural waters. Mar. Chem., 50, 21–39.]) in which case the organic and inorganic ligands could compete effectively for Fe. Different values of organic alpha and the occurrence of two organic ligand classes were consistent with differences in hydrography. South of the Polar Front, the least organic complexation occurred (organic alpha = $10^{12.4}$, organic complexation around 80%), where the highest chlorophyll *a* concentrations were measured.

Keywords: Iron; Chemical speciation; Southern Ocean; Seawater

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1. Introduction

For both total Fe and Fe(III) speciation determinations, sensitive and reliable methods have been developed and successfully used (Rue and Bruland, 1995; Van den Berg, 1995; Gledhill and Van den Berg, 1994; Obata et al., 1993). However, the role of iron speciation in the primary productivity in so-called High Nutrient, Low Chlorophyll (HNLC) regions is still not quite clear (de Baar and Boyd, 1998; Wells et al., 1995). Here we report the first assessment of organic complexation in the Southern Ocean, the largest and most important HNLC region (Coale et al., 1996; Cooper et al., 1996).

It is not yet possible to define the bio-available Fe fraction and it is not known how and in what form algae take up Fe (Wells et al., 1995). Johnson et al. (1994) found in the equatorial Pacific that colloidal Fe was dissolved by photo-reduction during daytime, especially around midday. Iron was subsequently oxidized and taken up as dissolved Fe(III). It appeared, although the authors did not elaborate, that also chelated Fe could be photo-reduced. They found that particulate Fe was most likely refractory and non reducible.

In the present paper we report measurements of the speciation of iron in samples from the Pacific region of the Southern Ocean between 58° and 68°30′S along the 90°W meridian. The Fe speciation measurements were part of a research project on dissolved and dissolvable iron concentrations (de Baar et al., 1998) and shipboard Fe bioassay experiments investigating the response of phytoplankton to additions of 2 nM Fe (Timmermans et al., 1998 and Van Leeuwe et al., 1998a,b).

Iron speciation was measured with competitive ligand equilibration adsorptive cathodic stripping voltammetry (CLE ACSV) (Gledhill and Van den Berg, 1994) using 1-nitroso-2-naphthol as competing ligand. Since it is still unknown whether plankton species can utilize colloidal Fe, dissolved chelated Fe or purely inorganic dissolved Fe, we had chosen to use unfiltered samples for the speciation measurements. This would also avoid conceivable artifacts due to lysis of cells, adsorption and desorption and contamination. Instead of total dissolved Fe we used total dissolvable Fe measured by flow injection analysis (FIA) in unfiltered acidified (pH 1.6) sea water samples (Landing et al., 1986; Obata et al., 1993). Dissolved Fe (< 0.4 and < 0.2 μm) concentrations can be found in de Baar et al. (1998). Latter data show that in retrospect clean filtration would have been possible also for this study, however, artifacts due to lysis would still be a problem since the normal procedure, filtering under nitrogen pressure (0.5–0.45 bar) (Rue and Bruland, 1995, Gledhill and Van den Berg, 1994), may rupture plankton cells. The results of the speciation measurements are compared with chlorophyll *a* concentrations and the hydrography of the area.

2. Sampling and methods

2.1. Research area

Samples were collected during the ANT XII/4 cruise on board the RV Polarstern from 21 March until 14 May 1995. The research area was situated in the Pacific part of the Southern Ocean and stations were visited following a transect along the 90°W meridian from North to South (58°–68°30′S). During this survey different water masses were sampled including those typical for the Antarctic Circumpolar Current, the Polar Front and the Bellingshausen Sea. Stations and positions of the survey are given in Fig. 1. At stations 152 and 199, no CTD and chlorophyll *a* were sampled and for comparison the data from stations 154 and 186 were used (Fig. 1 caption).

2.2. Sampling

Acids for cleaning and analysis, hydrochloric and nitric acid (Merck), were three-fold subboiling quartz distilled and stored in Teflon bottles.

Samples were collected with a specially designed winch equipped with a 1000 m Kevlar cable. Go-Flo samplers (12-l volume each) were used throughout. These were extensively cleaned with 0.1 M HCl, rinsed with Milli-Q water (> 18 MΩ cm, Fe concentration 0.58 ± 0.07 nM ($n = 10$)) and stored in plastic bags. Shortly before use they were filled with sea water, acidified to pH 2, and left to stand overnight. Before sampling they were rinsed with sea water again. Attached to the Kevlar cable they were

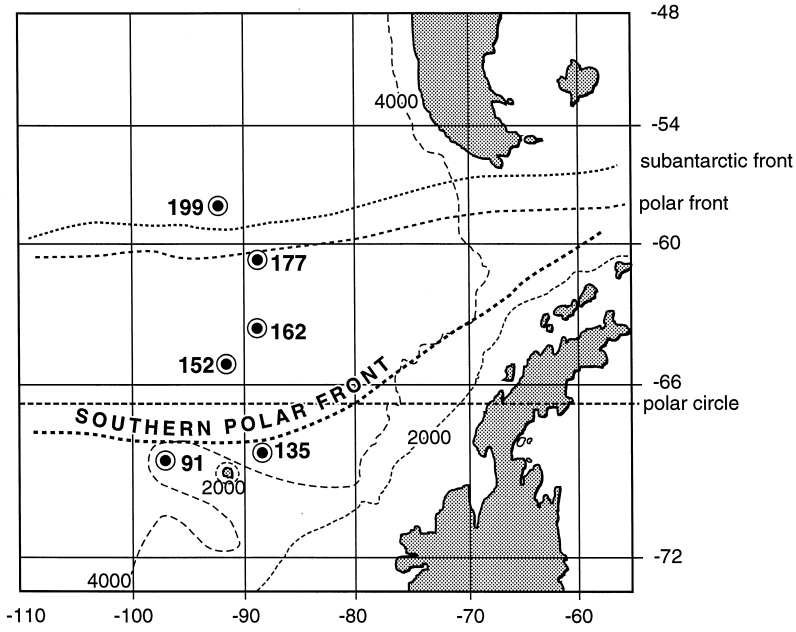


Fig. 1. Area of investigation with the sampled stations. The typical positions of the fronts are indicated. The positions of the stations are: 199 (57.58°S, 91.51°W); 177 (60.58°S, 89.29°W); 162 (63.58°S, 89.33°W); 152 (65.23°S, 91.10°W); 135 (68.15°S, 89.23°W); 91 (68.30°S, 97.10°W). Not shown: 186 (59.27°S, 89.31°W) and 154 (65.08°S, 90.41°W).

submerged to collect water samples at 25, 50, 75, 100, 150, 200, 300, 400, 600 and 800 m depth. Messengers made of teflon were used to close the Go-Flo samplers. Upon recovery, the bottles were directly attached to storage boxes, which were fixed outside a class 100 clean laboratory container. Teflon tubes through the container wall were attached to the Teflon valves of the Go-Flo samplers.

After pressurizing the Go-Flo samplers with 0.5 bar nitrogen, the valves were opened and high density polyethylene (200 ml, HDPE) sample bottles conditioned with sea water, were rinsed twice, and subsequently filled. These sample bottles had been thoroughly cleaned before use as follows. They were treated with a detergent, rinsed with Milli-Q water and cleaned by subsequent soakings for one day in hot 6 M HCl and hot 6 M HNO_3. The bottles were rinsed with Milli-Q water, dried in a laminar flow bench and, after drying, wrapped in plastic bags. Unpacking of the bottles was done in laminar flow benches inside the clean container unit. All material used during the analytical procedure was cleaned and treated in the same way as the sample bottles. Samples which were analyzed onboard the ship, were stored in a refrigerator at 8°C until analysis. Those to be analyzed, in the laboratory, after the cruise were stored frozen at −20°C.

2.3. Instrumentation and methods

2.3.1. Flow injection analysis (FIA-CL)

Total dissolvable Fe concentrations were measured in unfiltered acidified (pH 1.6) sea water samples, using flow injection analysis (FIA) which was adapted from the method by Obata et al. (1993). This method is based on the in-line preconcentration on a column of 8-hydroxyquinoline immobilised on hydrophobic vinyl polymer (Landing et al., 1986), followed by chemiluminescence (CL) detection using the iron catalyzed oxidation of luminol by hydrogen peroxide. Typical blank values and detection limits (defined as 3 times the standard deviation of the blank) were equivalent to 0.05 nM Fe and 0.015 nM Fe, respectively ($n = 55$). The method was validated using reference sea water NASS-4 (certified 1.88 ± 0.29 nM Fe). During the cruise 1.81 ± 0.15 nM ($n = 4$) was found for this reference sample. The

precision was found to be within 5% relative standard deviation in the whole range of concentrations (0.05–2 nM Fe).

For all samples the fraction < 0.4 μm was measured, total dissolvable Fe was measured in stations 199, 162 and the deep section of station 177. Total dissolvable Fe for the other samples was obtained by multiplying the fraction < 0.4 μm with 2–6, depending on the depth (> 300 m multiplying with 2) and differences between total dissolvable Fe and < 0.4 μm of neighboring stations (station 91, 75 m [Fe] < 0.4 μm $= 0.15$ nM total dissolvable estimated to be 0.21; station 135, 800 m [Fe] < 0.4 μm $= 0.47$, total dissolvable estimated to be 0.72 nM; station 152, 100 m [Fe] < 0.4 μm $= 0.16$, total dissolvable estimated to be 0.57; station 177 at 50 m depth [Fe] < 0.4 μm $= 0.06$, total dissolvable estimated to be 0.25). Errors made by these interpretations in the estimations of the ligand characteristics is minimal, this is shown in the discussion.

A detailed description of the method as well as results from cruise ANT XII/4 were given by de Baar et al. (1998).

2.3.2. Nutrients and CTD

Nutrients were determined on board using TRAACS 800 Automated Analysers (Grasshoff, 1983). Detection limits were 0.02 μM for phosphate, 0.02 μM for nitrate and 0.1 μM for silicate. Chlorophyll *a* was measured according to Holm-Hansen et al. (1965). Salinity and temperature were measured with a Sea-bird CTD.

2.3.3. Electrochemical measurements

The voltammetric equipment consisted of a Metrohm 663 VA Stand, with a hanging mercury drop electrode (HMDE) working electrode and Eco-Chemie μAutolab voltammeter. The potentiostat setting as well as stirring, de-aeration, timing and the HMDE were computer controlled (General Purpose Electrochemical system; version 3.2, 1993). A stock solution of 0.02 M 1-nitroso-2-naphthol (NN, Fluka Chemie) was prepared in methanol (quartz distilled), and stored in a Teflon bottle. Fresh solutions were made every 2 months. An aqueous solution of 1 M piperazine-*N*,*N*-bis-2-ethane sulphonic acid (PIPES, Merck) was prepared in 0.5 M ammonia. Ammonia was prepared by saturating Milli-Q water with ammonia gas. Iron was removed from the PIPES buffer by shaking for 8 h with 0.1 mM MnO_2 and subsequent filtration over a pre-cleaned 0.45 μm polycarbonate filter. An aqueous stock solution of 1 M tris(hydroxymethyl)aminomethane (TRIS, Merck) was prepared in 0.5 M quartz distilled hydrochloric acid. This buffer was cleaned by addition of 0.1 mM NN and passing through a Seppak C18 column by gravity flow. A 0.7 M stock solution of hydrogen peroxide (Baker Grade) was prepared by diluting 30% w/v and was cleaned by addition of 0.01 M PIPES and equilibration with 0.1 mM NN before passing through a pre-cleaned Seppak C18 column by gravity flow. Standard solutions of iron were prepared by diluting a solution of 1000 mg Fe l^{-1} (Atomic Absorption Spectroscopy standard) and acidifying it to pH 2. Two standards were used, 1.57 μM and 220 nM. In order to avoid evaporation, crystallization and degradation, all prepared solutions were stored in a refrigerator at 8°C. The mercury (Fluka Chemie) had to be filtered every 2 months to remove mercury oxide.

2.3.4. Determination of iron speciation using competitive ligand equilibration adsorptive cathodic stripping voltammetry (CLE-ACSV)

NN was used as added ligand according to procedures of Gledhill and Van den Berg (1994). However, sodium dodecyl sulphate, which was used by Gledhill and Van den Berg (1994), was not added to the samples. Fe titrations were carried out on different samples from certain depths taken at stations 91, 135, 152, 162, 177 and 199 (25 m depth) on board ship. Samples encompassing a depth profile were collected at station 199. These were frozen (at -20°C) and analyzed after the cruise. On shipboard, eleven 10 ml aliquots were taken from the original 200 ml of unfiltered sea water and pipetted into 30 ml PTFE bottles. PIPES buffer was added to obtain a concentration of 0.01 M, pH 6.9. NN was added to get a final concentration of 1 μM. Iron was added in 10 increments of 1.8 nM. The bottles were stored at 8°C for a period of at least 8 h. After equilibration and allowing the mixtures to warm to room tempera-

ture, hydrogen peroxide was added to give a concentration of 25 μM. The iron concentration was measured in each sub-sample.

The analytical procedure was as follows. The 10-ml samples were poured into the Teflon voltammetric cell. The solution was de-aerated with nitrogen (4.5) for 5 min. Deposition was allowed for 15 s at −0.15 V while stirring the solution. Then, the potential was adjusted to −0.35 V for 1 s to pre-reduce impurities in and on the surface of the mercury drop. The stirrer was stopped and a quiescence period of 9 s was allowed. Finally, a scan took place from −0.35 V to −0.65 V with a fast linear sweep wave form at a scan rate of 50 mV s^{-1} and a step potential of 4 mV. The reduction peak for iron appeared at −0.475 V. Every scan was repeated twice without purging and the average of the three peak heights was used for calculations.

Between titrations the electrodes and polarographic cells were equilibrated with low iron containing sea water (< 0.3 nM) with 1 μM NN and 0.01 M PIPES. Because the results were obtained at pH 6.9, they were recalculated to the natural pH 8.1 (Gledhill and Van den Berg, 1994) using $10^{11.9}$ for the inorganic side reaction (see data treatment).

The samples of the profile from station 199 were analyzed after the cruise in the home laboratory. In contrast with the method described above, a TRIS buffer (0.01 M) was used at pH 8.1 (Van den Berg, 1995). These Fe titrations consisted of 11 additions starting with 0.25 nM and gradually increasing towards 22.0 nM (0.25, 0.5, 1, 2, 4, 6, 8, 10, 14, 18, and 22 nM).

2.3.5. Data treatment

Titration data were used to calculate the conditional stability constant (K') and the concentrations of the dissolved organic ligands ($[L_t]$). The constant K' is conditional because it comprises the activity coefficients of various reactants in the non-ideal solution of sea water at given salinity and ionic strength (Millero and Schreiber, 1982). The following assumptions and definitions were applied. The inorganic side reaction (α_{inorg}) of Fe(III) was assumed to be $10^{11.9}$ according to Millero et al. (1995). K' was calculated with respect to Fe^{3+}. Ligand concentrations are expressed in equivalents of M Fe (Eq). It was assumed that complexes exist in a 1:1 coordination and that the Langmuir isotherm was a valid model to describe complexation.

The Langmuir isotherm was used in three forms. By a nonlinear fit (Gerringa et al., 1995):

$$[\mathrm{MeL}] = \frac{[L_t] * K' * [\mathrm{Me}^{x+}]}{1 + K' * [\mathrm{Me}^{x+}]} \quad (1)$$

by the Van den Berg/Ružić linearization (Van den Berg, 1982; Ružić, 1982):

$$\frac{[\mathrm{Me}^{x+}]}{[\mathrm{MeL}]} = \frac{[\mathrm{Me}^{x+}]}{[L_t]} + \frac{1}{K' * [L_t]} \quad (2)$$

and by the Scatchard (1949) linearization,

$$\frac{[\mathrm{MeL}]}{[\mathrm{Me}^{x+}]} = K' * [L_t] - K' * [\mathrm{MeL}] \quad (3)$$

The Scatchard linearization has its constraints for calculations. It can be used however, to detect more than one ligand (Buffle, 1988; Rue and Bruland, 1995; Ružić, 1996).

In order to calculate complexation characteristics it is common to use the Van den Berg/Ružić linearization (Coale and Bruland, 1990; Wu and Luther, 1995; Van den Berg, 1995). The results using Eq. (2) approach those from the nonlinear fit of the Langmuir equation, but are more susceptible to outliers or data points that do not closely follow the Langmuir isotherm. Moreover, standard errors of the estimated parameters, K' and $[L_t]$, cannot be calculated consistently with the Van den Berg/Ružić linearization (Gerringa et al., 1995).

With the nonlinear fit (Eq. (1)) data pairs of $[\mathrm{Me}^{x+}]$ and [MeL] resulting from ACSV measurements are fitted directly. The nonlinear fitting routine of the package SYSTAT was used (Wilkinson et al., 1992). This performs a least-squares fit with the Simplex algorithm. Asymptotic standard errors and the correlation between the parameters have been computed from the Hessian matrix. Contours of the loss function (sum of squared deviations of data

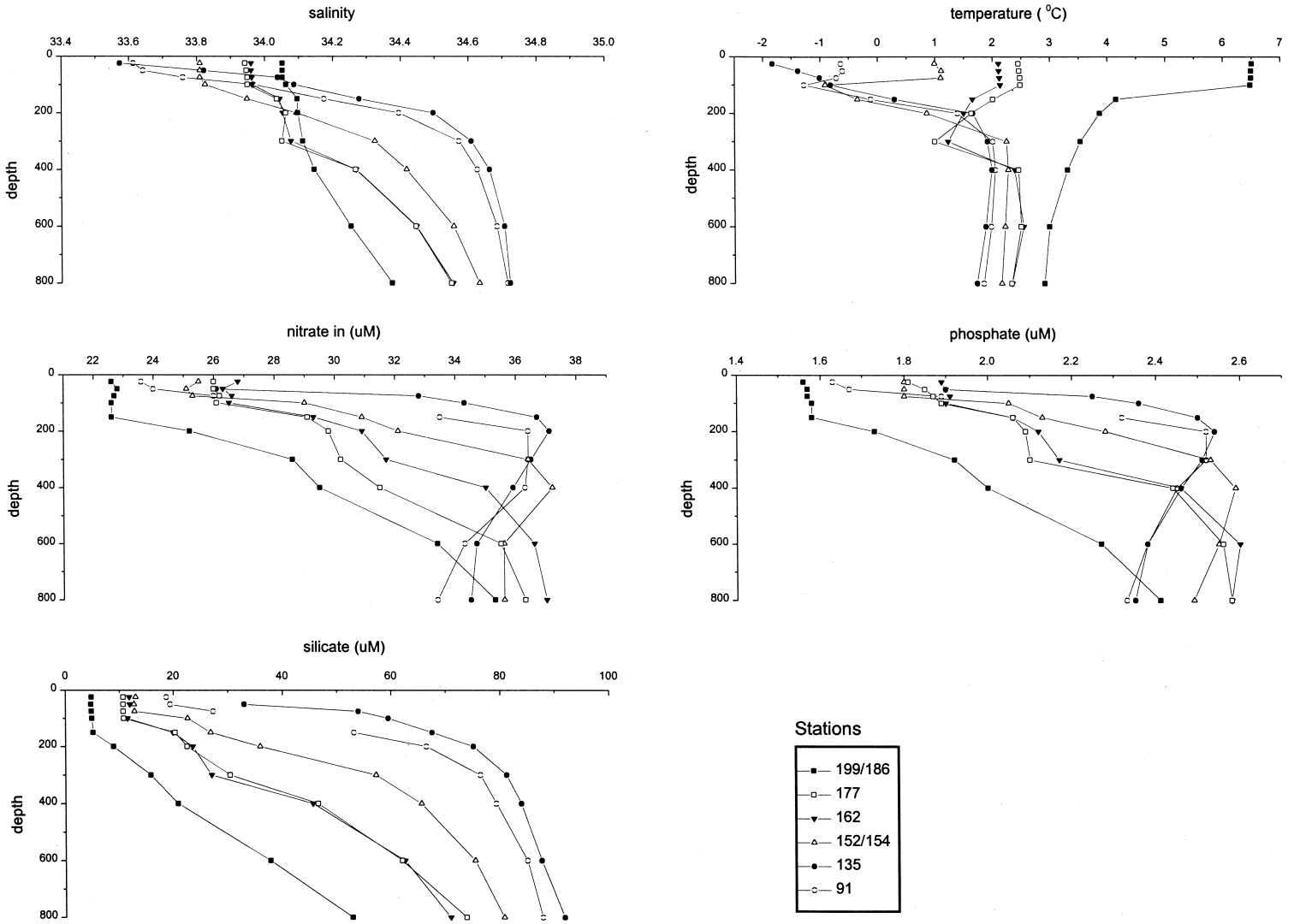


Fig. 2. Salinity, temperature (°C) and concentrations of the nutrients (μM) with depth. Salinity and temperature are measured at station 186 (59.27°S, 89.31°W) instead of station 199 and at station 154 (65.08°S, 90.41°W) instead of station 152.

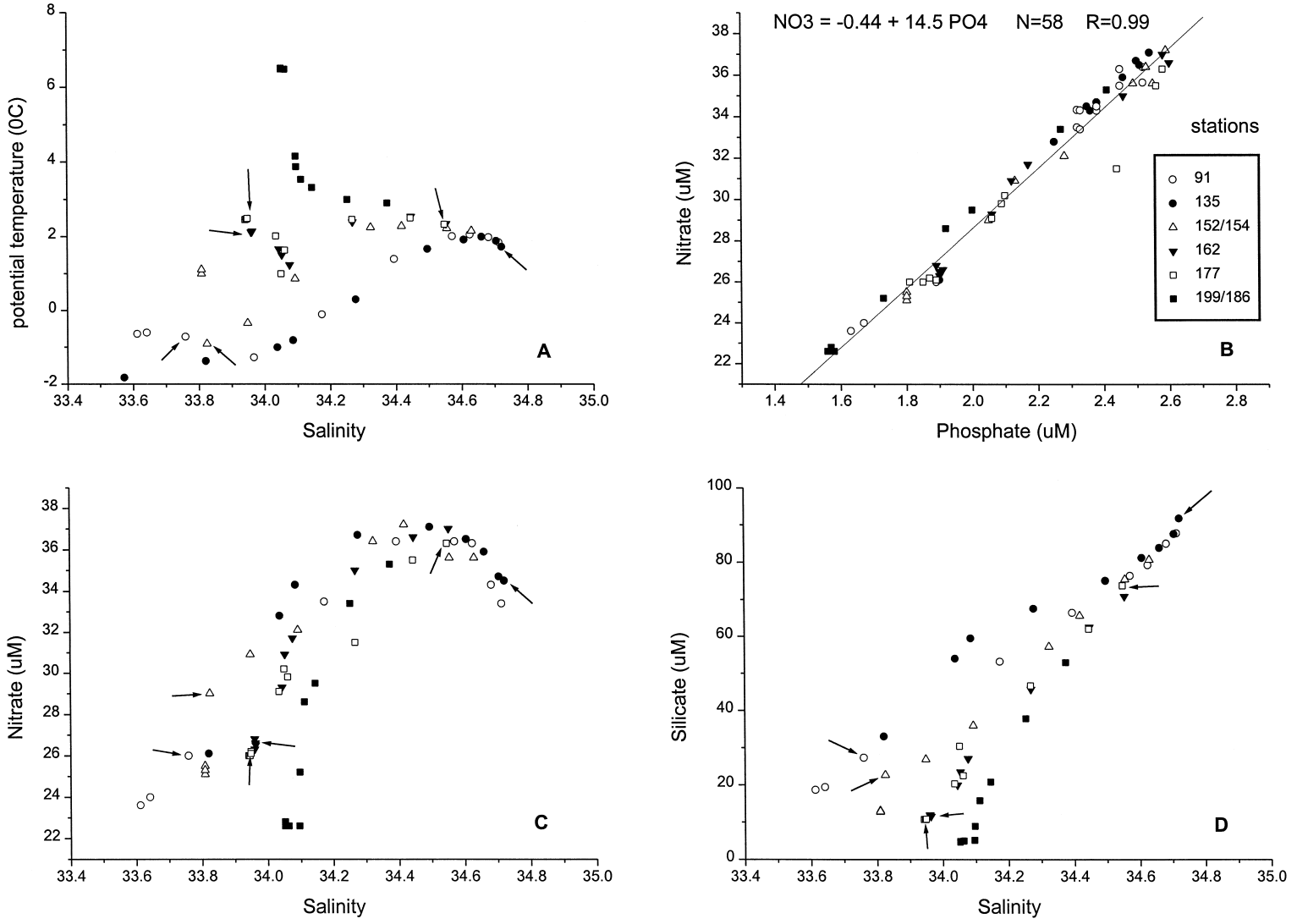


Fig. 3. Property plots of (A) temperature versus salinity; (B) nitrate versus phosphate; (C) nitrate versus salinity; (D) silicate versus salinity. The samples for which Fe complexation was measured are indicated in the graphs by arrows, for all samples at station 199 complexation is measured, these are not separately indicated by arrows.

Table 1
Total dissolvable Fe (nM) and ligand characteristics, calculated with three forms of the Langmuir equation for samples from stations 91, 135, 152, 162 and 177 (measured at pH = 6.9 and recalculated to pH = 8.1), total dissolvable Fe in station 91 (75 m) is assumed to be 2 times [Fe] < 0.4 μm, for station 135 (800 m) 2 times, for station 152 (100 m) 3.5 times, and for station 177 (50 m) 6 times (from de Baar et al., 1998)

Station	Depth (m)	Dissolvable, Fe (nM)	Non-linear log K'	95% conf.	L_t nEq	95% conf.	Van den Berg/Ružić log K'	L_t nEq	R^2	Scatchard log K'	L_t nEq	R^2	Nonlin log alpha organic	Nonlinear % org. complexed	Berg/Ružić log alpha organic	Berg/Ružić % org. complexed	Scatchard log alpha organic	Scatchard % org. complexed
91	75	**0.21**					21.93	1.08	0.998	21.79	1.12	0.978			12.2	66.99	12.84	89.7
135	800	**0.72**	**20.6**	0.27	**5.43**	0.86	20.93	4.79	0.981	20.58	6.09	0.522	12.4	76	12.11	61.91	12.35	73.65
152	100	**0.16**	**20.77**	0.33	**3.52**	0.5	21.39	3.19	0.967	20.7	3.92	0.656	12.44	77.48	12.83	89.48	12.29	71.21
162	50	**0.57**	**21.24**	0.22	**7.17**	0.44	21.72	7.46	0.996	21.34	7.82	0.82	13.25	95.69	12.85	98.51	13.23	95.56
177	50	**0.25**	**21.13**	0.35	**5.57**	0.5	20.94	5.8	0.994	21.11	5.8	0.554	12.89	90.64	12.88	90.53	12.87	90.4
177	800	**0.27**	**21.25**	0.2	**13.08**	0.7	21.22	13.27	0.998	21.29	12.87	0.939	13.39	96.84	13.67	98.33	13.4	96.9

Table 2
Total dissolvable Fe (nM) and ligand characteristics for station 199 according to the nonlinear regression of the Langmuir equation, estimated with the Van den Berg/Ružić linearization and estimated with the Scatchard linearization

Nonlinear

Depth (m)	Dissolvable Fe (nM)	1 ligand						2 ligands									
		log K'	95% conf.	L_t nEq	95% conf.	[Fe^{3+}] (M)	Inorg Fe (M)	log K'_1	95% conf.	L_{t_1} nEq	95% conf.	log K'_2	95% conf.	L_{t_2} nEq	95% conf.	1 ligand log alpha	2 ligands log alpha
25	0.14	21.29	0.12	5.85	0.15	1.15×10^{-23}	9.11×10^{-12}									13.06	
50	0.62	21.51	0.3	5.86	0.65	3.14×10^{-23}	2.49×10^{-11}									13.28	
75	0.39	21.81	0.21	2.25	0.22	2.54×10^{-23}	2.02×10^{-12}									13.16	
100	0.38	21.08	0.22	3.42	0.39	7.75×10^{-23}	6.15×10^{-11}									12.61	
150	0.28	21.85	0.19	4.87	0.42	7.84×10^{-24}	6.31×10^{-12}									13.54	
200	0.48	21.54	0.24	6.18	0.75	2.16×10^{-23}	1.72×10^{-11}									13.33	
300	0.55	21.27	0.16	7.2	0.6	4.10×10^{-23}	3.26×10^{-11}									13.13	
400	0.68	21.61	0.13	7.78	0.59	2.15×10^{-23}	1.70×10^{-11}	22.46	0.51	2.53	1.85	21.12	0.28	5.7	1.75	13.5	13.91
600	0.57	21.13	0.14	10.69	1.02	3.74×10^{-23}	2.97×10^{-11}									13.16	
800	0.72	21.18	0.15	12.3	1	3.63×10^{-23}	2.89×10^{-11}	22.38	1.45	1.81	50	20.99	0.31	10.9	3.2	13.27	13.73

Berg/Ružić depth (m)	log K'	L_t nEq	R^2	log K'_1	L_{t_1} nEq	log K'_2	L_{t_2} nEq	1 ligand log alpha	2 ligands log alpha
25	21.48	5.68	0.999					13.23	
50	21.87	5.56	0.987					13.62	
75	21.88	2.18	0.995					13.22	
100	21.03	3.19	0.984					12.53	
150	22.16	4.63	0.997					13.83	
200	21.58	5.85	0.989					13.35	
300	21.34	6.93	0.996	21.96	2.44	21.52	4.42	13.18	13.57
400	21.72	7.87	0.999	22.2	4.27	21.57	3.65	13.62	13.91
600	21.1	10.32	0.995	21.93	1.94	21.42	8	13.11	13.57
800	21.36	11.84	0.997	22.08	4.78	21.35	7	13.43	13.86

Scatchard

25	21.24	5.93	0.937					13.01	
50	21.8	5.86	0.397					13.57	
75	21.63	2.41	0.779					13.01	
100	21.66	4.55	0.509					13.32	
150	21.73	5.04	0.823					13.43	
200	21.39	6.72	0.614					13.22	
300	21.32	7.09	0.867	22.11	1.94	21.11	5.71	13.17	13.51
400	21.88	7.28	0.925	22.2	4.5	21.26	3.9	13.74	13.89
600	21	11.69	0.697					13.07	
800	21.56	10.6	0.835	22.19	4.2	21.06	8.64	13.58	13.87

from the model) in the L_t–K' plane are regularly elliptic, adding confidence to the values of the asymptotic standard errors (Gerringa et al., 1995). This method can easily be extended to models including more than one ligand (Eq. (4)):

$$[\mathrm{MeL}]_t = \frac{[L_t]1 * K'1 * [\mathrm{Me}^{x+}]}{1 + K'1 * [\mathrm{Me}^{x+}]} + \frac{[L_t]2 * K'2 * [\mathrm{Me}^{x+}]}{1 + K'2 * [\mathrm{Me}^{x+}]} \quad (4)$$

It should be noted, however, that two extra parameters need to be estimated for every extra ligand to be considered. Estimation can become difficult and unstable when ligands are similar in K' value, when K' values are at the extremes of the detection window, or when insufficient data are available. (Gerringa et al., 1991, 1995).

The calculation of two ligands with the linearized Langmuir equations is executed in a simple way. The plots are divided in two linear parts representing the two ligands groups. On these two linear parts linear regressions are applied separately (Van den Berg personal communication). We assume that Rue and Bruland (1995) made the same simplification for the determination of two ligands by using the Scatchard linearization.

3. Results

3.1. Hydrography

The northern part of the research area (station 199) is north of the Sub Antarctic Front (SAF) and Polar Front (PF) (Whithworth, 1988), and is characterized by relatively high surface temperature and high salinity (Fig. 2). The SAF and PF are thought to lie between stations 199 and 177 (Figs. 1–3). Due to a 3-day lasting hurricane the wind mixed layer at station 199 extended until 125 m depth. Below the sharp thermocline at this depth the temperature gradually decreases until 3°C at 800 m. From the salinity–temperature and salinity–nutrient plots at station 199 (Fig. 3) two different water layers can be distinguished. One in the surface layer extending until 200–300 m is separated from the underlying layer (Fig. 3A).

Temperature and salinity profiles from stations 162 and 177 in the Antarctic Zone (AZ) are almost identical. Below a well-mixed near-surface layer of 125 m, a distinct temperature minimum of 1°C and 34.1 S at 300 m is found, which is characteristic for Antarctic Intermediate Water (AAIW). Below the temperature minimum, salinity increases gradually and this water is a tongue of the Pacific Deep Water (PDW), one of the source terms of the Circumpolar Deep Water (CDW) (Whithworth, 1988). More southward, passing the Southern Polar Front (SPF) (Read et al., 1995), one finds the transition into the Bellinghausen Sea with lower surface temperatures and lower salinities due to melt water of ice and snow. Stations 91 and 135 are situated south of the SPF.

A temperature minimum of -1°C is found at 75–100 m depth at stations 91 and 152. This is the winter water, which is flowing in northward direction and there forms the AAIW (Whithworth, 1988). Below this winter water at 100 m we find a layer of about 100 m thickness which is a mixture of surface water with PDW, as inferred from a phosphate and nitrate maximum (see below), and below this layer is the CDW with a salinity > 34.5. The temperature minimum found at the surface at station 135, is due to the fact that during sampling, the surface was completely covered with ice and there was hardly any wind, thus preventing the development of a wind mixed surface layer. Hydrographical characteristics at this station were identical to those found at station 91. The salinity–temperature plot (Fig. 3A) shows that at all stations south of the SAF and PF, CDW is present with a temperature of 2°C and a salinity > 34.5 S. From the temperature–salinity plot (Fig. 3A) it can be concluded that we are dealing with at least three water masses, the winter water gradually

Fig. 4. Plots of the Van den Berg/Ružić and Scatchard linearizations of the Langmuir isotherm for Fe complexation for samples from station 199. At 25, 50, 75, 100, 150, 200 m, 300, 400, 600 and 800 m depth.

sinking in northward direction and forming AAIW, the PDW and for the stations situated in the Bellinghausen Sea and in the AZ the CDW.

3.2. Nutrients

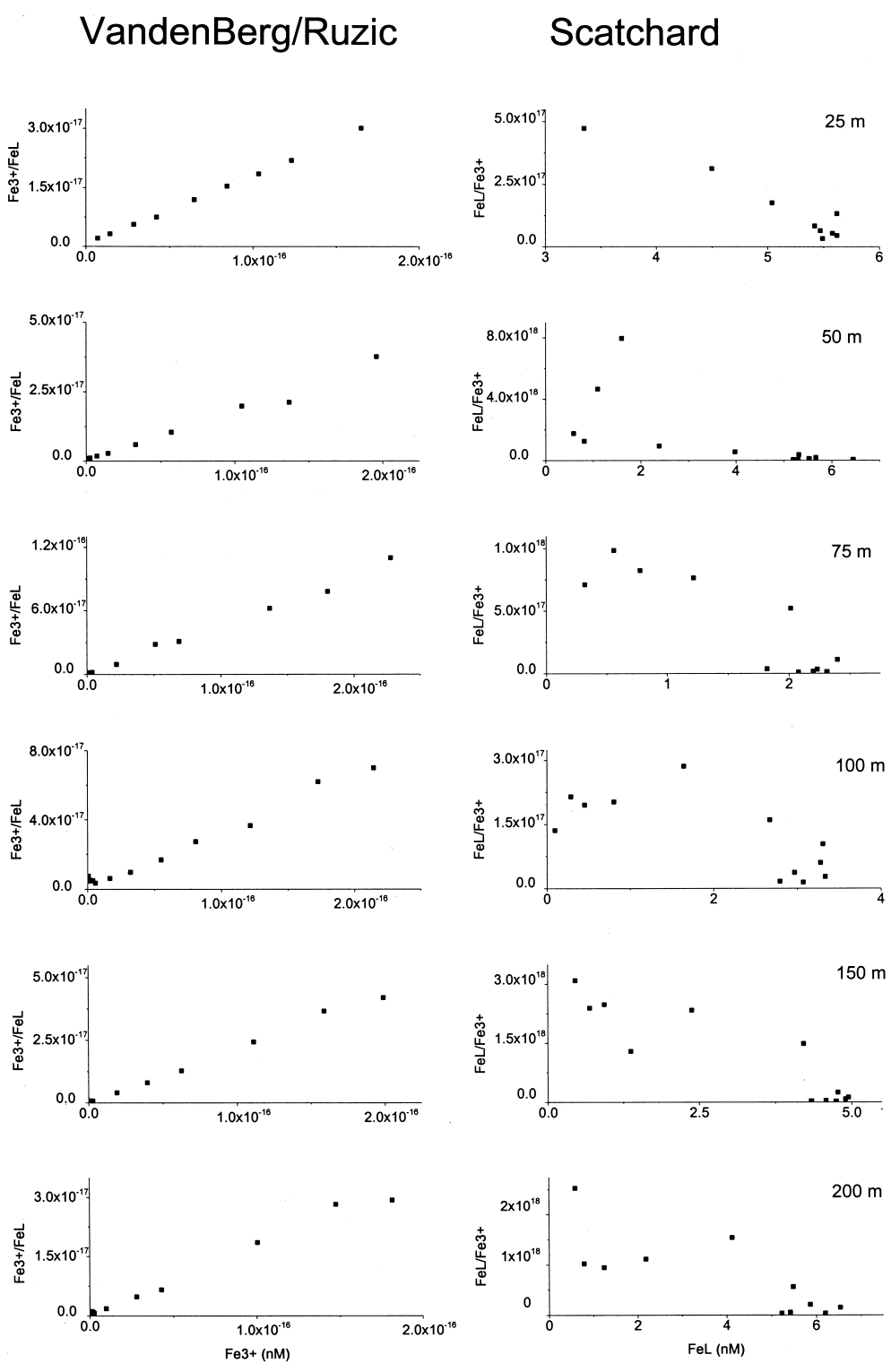
Phosphate and nitrate show some surface depletion, with strong gradients at stations 91, 135 and 152 in the Bellinghausen Sea (Fig. 2). At these stations also a sub-surface maximum for phosphate and nitrate is found at 200 m depth for stations 91 and 135 and at 400 m depth at station 152. This is in contrast to stations 162, 177 and 199 more northwards, where concentration gradients are smaller in the upper 800 m and no sub-surface maximum could be observed. From comparison with GEOSECS (1981) it is obvious that at these stations the nutrients maximum is situated below 700 m, and so just detectable at our lowest sampling depths. This subsurface maximum for phosphate and nitrate is found at a salinity 34.5 and represents a small tongue of PDW. Below this level, the nutrients show concentrations indicative for CDW. The phosphate/nitrate relation of all stations is plotted in Fig. 3. This relationship shows that although we are dealing with different water masses, the relative proportion of these nutrients is fairly uniform. The ratio of 14.5 is slightly lower than the ratio of 15–16 estimated as average for oceanic waters by Redfield et al. (1963) and Fanning (1992), but similar to that found in the Weddell Sea (Nolting and de Baar, 1994). This generally lower N/P ratio of the Antarctic Ocean is well known and the possible underlying mechanisms were discussed elsewhere (de Baar et al., 1997). Phosphate, nitrate and silicate concentrations in the upper water layer are lower at station 199 at the same salinities compared to those at the other stations Fig. 2. This confirms the conclusion that the upper water layer at station 199 is clearly different and separated from that at the other stations, which are situated south of the SAF and PF.

3.3. Fe complexation

The calculations of the complexation characteristics assuming the existence of only one ligand yield a conditional stability constant between 10^{21} and $10^{21.85}$ (Tables 1 and 2). Values obtained by the original method of Gledhill and Van den Berg (1994) at pH = 6.9 (stations 91–177 and 25 m depth of station 199), do not differ from those determined at pH = 8.1 (station 199 below 25 m depth) (Van den Berg, 1995). The stability constants are comparable to the K' value of the weakest ligand found by Rue and Bruland (1995), $K' = 10^{21.48}$, in the central north Pacific and to the highest values found by Gledhill and Van den Berg (1994) in the Menai Straits and the Atlantic Ocean, $K' = 10^{18.8}$–$10^{21.5}$, and by Van den Berg (1995) in the Mediterranean, $K' = 10^{19.4}$–$10^{22.4}$.

The ligand concentrations vary between 0.7 and 13 nEq Fe l^{-1} (Tables 1 and 2). The ligand concentration is at least 3 times, and generally more than 10 times, the concentration of the ambient total dissolvable Fe concentration. It is rather low at the southern stations (91, 135, 152). At station 199 the ligand concentration is 5 neq Fe l^{-1} near the surface, decreases between 75 and 150 m depth and gradually increasing with depth in the water column.

The three forms of the Langmuir equation in general do not result in significantly different K' and L_t values; exceptions with some difference between the methods are found at stations 152, at 100 m depth and at station 199, at 100 m depth. The R^2 values of the Scatchard linearization often are quite poor (< 0.9). This method was used to indicate the existence of more than one ligand. This could only be applied to data from station 199, due to the relatively large additions in the Fe titrations of the other samples treated on board of the ship. The Scatchard plots of the profile of station 199 show that below 200 m depth two ligands exist (Fig. 4), which is indicated by a departure from an otherwise straight line. This is confirmed by a close examination of the Van den Berg/Ružić plots, showing a curvature in the lower left part of this plot for those deeper samples (Buffle, 1988; Ružić, 1996). Unfortunately the sample at 600 m depth shows proof of the influence of slow kinetics of the complexation reaction in the data points in the linearized plots. Possibly, no equilibrium was reached between the added and the natural ligands (Ružić, 1996). Calculation of two ligands with the non-linear fit was successful for the samples at 400 and 800 m depth. Of course the error boundaries are rather large due to the few data points (12), but as shown in Fig. 5b the


VandenBerg/Ruzic
Scatchard
25 m
50 m
75 m
100 m
150 m
200 m
Fe3+/FeL
FeL/Fe3+
Fe3+ (nM)
FeL (nM)

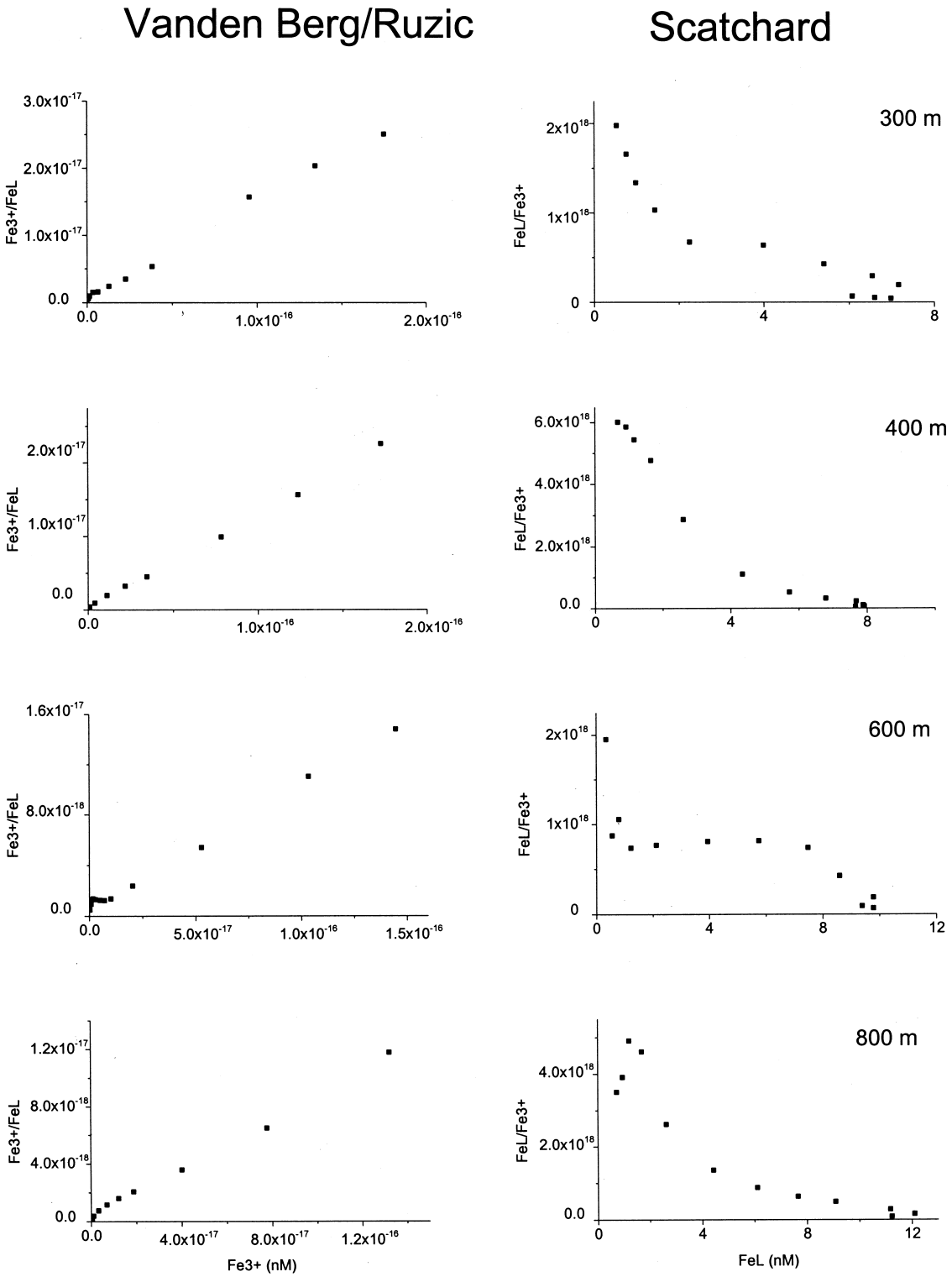


Fig. 4 (continued).

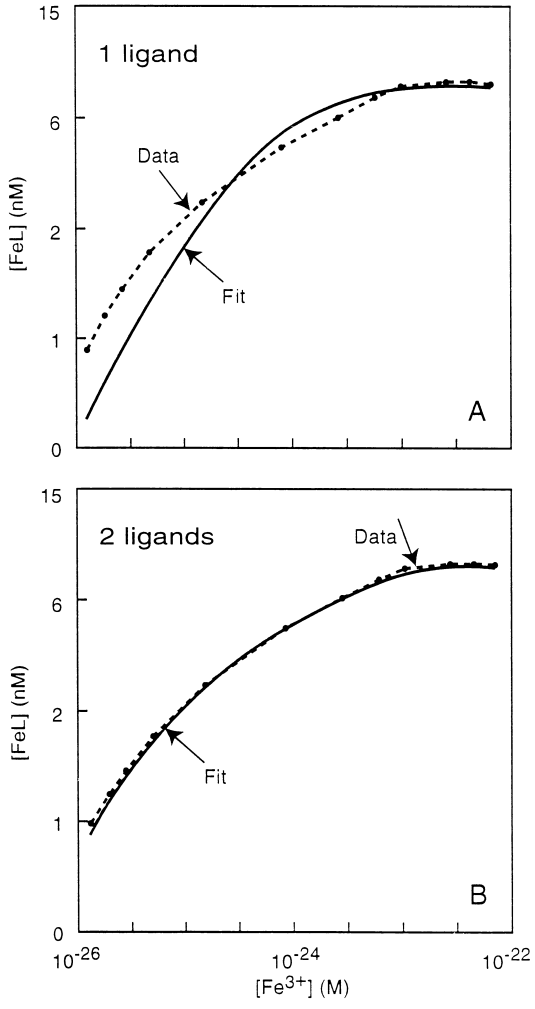


Fig. 5. Nonlinear fit of the Langmuir equation of the data from station 199 (400 m depth). A: assuming the existence of one organic ligand (Eq. (1)); B: assuming the existence of two organic ligands (Eq. (4)).

fit is perfect. The Van de Berg/Ružić fit could be used for all four samples, the Scatchard linearization could be used for the samples at 300, 400 and 800 m depth to calculate the parameters of two ligands (Table 2). Only those parameters estimated by the non-linear fit are calculated in a correct way. The K' values of the two ligand classes do not differ much from each other, the weakest is 10^{21}, the strongest $10^{22.4}$. The stronger ligand class is somewhat weaker than the stronger ligand found by Rue and Bruland (1995), $K' = 10^{23.1}$. This is possibly due to the difference in pre-treatment of the samples (unfiltered vs. filtered).

4. Discussion and conclusions

Results of speciation measurements of unfiltered samples give us information on the maximum capacity of material in seawater which can complex iron. This gives us a more realistic image of ionic Fe in equilibrium with all phases present in the environment of the phytoplankton, dissolved organic ligands, colloids and particles. If particulate Fe is indeed largely inert, like Johnson et al. (1994) indicate, the error we might make is a slight overestimation of the ligand concentration because the particulate Fe concentration in these waters is low (de Baar et al., 1998) and because truly inert Fe will not be measured in that case as total dissolvable Fe. Moreover the error will be minor since we prefer the use of the organic alpha (product of conditional stability constant K' and the ligand concentration $[L_t]$) as a measure for organic complexation. de Baar et al. (1998) measured in the same area in the upper 100 m that total dissolvable Fe was 3 to 6 times dissolved Fe (< 0.4 μm) and below 100 m total dissolvable Fe was 2 times dissolved Fe. In the worst case, when 5/6 of the total dissolvable Fe (0.62 nM) is particulate, the measured ligand concentration of 5.86 nEq of Fe (station 199, 50 m depth, Table 2) must in reality be 5.36 nEq of Fe. This results in an organic alpha of $10^{13.22}$ instead of $10^{13.28}$. Thus possible differences in the results will be negligible, especially when the organic alpha is used to characterize organic complexation.

Fig. 6 shows the percentages of organic complexation found in the profile of station 199. In Table 1 the percentages of organic complexation are given for the other stations. The organic complexation is lowest at the southern stations 91, 135 and 152 and at 100 m depth of station 199. Here, rather large differences can be seen among the three different applications of the Langmuir isotherm (Table 1, Fig. 6). This is due to the fact that the organic alpha is within one order of magnitude of the inorganic alpha $10^{11.9}$ (Millero et al., 1995). When the values for inorganic and organic alpha's are close to each other the organic and inorganic ligands really compete for

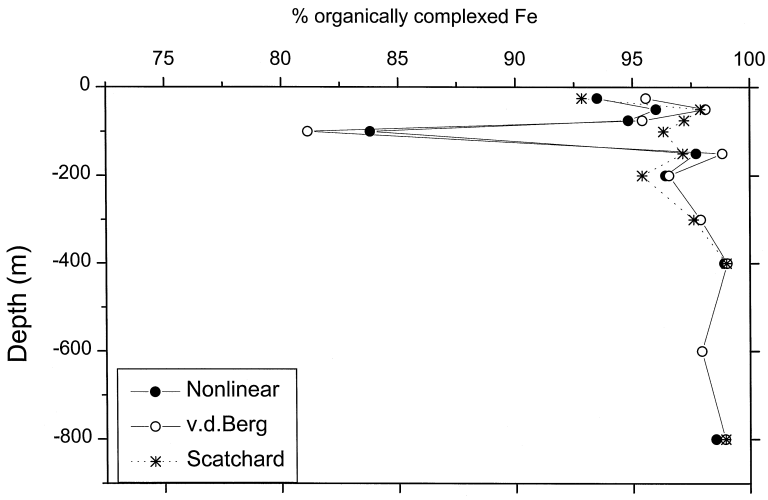


Fig. 6. The percentage of Fe which is organically complexed, according to the three forms of the Langmuir equation, as a function of depth for station 199.

Fe. Indeed, the organic alpha values (Tables 1 and 2) are within one order of magnitude of the inorganic alpha for the mentioned samples with lowest organic complexation. We used a relative high inorganic alpha ($10^{11.9}$, Millero et al., 1995) compared to other investigators. Wells et al. (1995) discussed the uncertainty of the existence of the various inorganic Fe(III) species, especially $Fe(OH)_3^0$, and summarized the then used alpha values to be in the 10^8–10^{10} range. Whereas Gledhill and Van den Berg (1994) used $10^{11.6}$, Rue and Bruland (1995) used 10^{10} and Rue and Bruland (1997) used 10^{11}. The latter authors showed that the percentages of organic complexation decreased when they used a higher value for the inorganic alpha. Using the value for inorganic alpha of Gledhill and Van den Berg (1994) only in the most southern stations (91 and 135) competition between organic and inorganic ligands would be present. The inorganic alpha value used by Rue and Bruland (1995) would not show any competition between the ligands. The percentage of organic complexation in station 135 would be 99.6% using 10^{10} as inorganic alpha (Rue and Bruland, 1995) and 76% (Table 1) using $10^{11.9}$. When organic and inorganic ligands really compete for Fe a relatively small variation in K' value has a large effect on the percentage of Fe complexed with organic ligands (Table 1, Fig. 6). It is therefore better when comparing results with work by others to use the organic alpha value, the binding potential of the organic ligands, than percentages of Fe which are organically complexed. In this manner the chosen value of inorganic alpha does hardly affect the interpretation.

Thus the lowest organic alpha values we found are $10^{12.4}$ for the southern stations, $10^{12.61}$ at 100 m depth at station 199, $10^{13.2}$ as a mean value for station 199 and $10^{13.9}$ in the presence of two ligands (Tables 1 and 2). These values are similar to the organic alpha value of Rue and Bruland (1995) (North Pacific) $10^{13.7}$, Rue and Bruland (1997) (equatorial Pacific) $10^{14.2}$ and Van den Berg (1995) $10^{11.5}$–10^{14}. Wells et al. (1995) already discussed the remarkable consistency of the organic ligand characteristics found in different regions. Now we know that also the Antarctic surface and deeper waters contain organic species with nearly the same organic complexation characteristics as those found in the Mediterranean, the Menai Street, the Atlantic Ocean, the North Pacific Ocean and the equatorial Pacific Ocean.

With the concentrations of the nutrients and the hydrography we could discriminate three water masses CDW, PDW and winter water forming AAIW and three different surface waters. In the southern stations, the organic alpha is low around $10^{12.4}$ in the surface layer (winter water at station 91 at 75 m

depth and winter water starting to form AAIW at station 152 at 100 m depth) as well as in the deeper water (CDW at station 135 at 800 m depth) (Fig. 3). Organic and inorganic ligands can compete effectively for Fe here, assuming that our choice of inorganic alpha is valid. In Fig. 7 the chlorophyll *a* concentrations are presented. The SAF and PF and the SPF can be recognized between stations 199 and 177 and stations 152 and 91, respectively (Figs. 1 and 7). Assuming that inorganic Fe is representative for overall biological availability of Fe, an assumption which is questionable, the region south of the SPF had most available Fe as well as elevated chlorophyll *a* abundance (Fig. 7). It is possible that the high chlorophyll *a* concentrations (Fig. 7) in the extreme south of the area are contaminated by ice algae, however Van Leeuwe et al. (1998b) also found higher chlorophyll *a* concentrations in this southern area though elevated only to a minor extent compared to the rest of the investigated area. They found that the phytoplankton community in this southern area was dominated by diatoms, albeit still in very low numbers compared to abundances in blooms elsewhere (Boyd et al., 1995; Savidge et al., 1995; Bathmann et al., 1997). Boyd et al. (1995) and Savidge et al. (1995) studied a bloom in the Bellingshausen Sea in the Austral spring of 1992, with real elevated numbers of phytoplankton immediately south of the SPF (then situated at 67.5°S), exactly where we find elevated concentrations of chlorophyll *a* and a relative low organic complexation of Fe.

Timmermans et al. (1998) and Van Leeuwe et al., (1998a,b) (Fig. 7) found very low concentrations of phytoplankton in the research area. Thus algae cannot influence the complexation characteristics in this region.

In the AZ, the region between the SAF and PF and the SPF, both relatively high and relatively low organic alpha values are found in the surface waters (alpha $= 10^{13.25}$ at station 162 at 50 m depth, alpha $= 10^{12.89}$ at station 177, at 50 m depth, alpha $= 10^{12.44}$ at station 152 at 100 m depth in winter water). At station 177 at 800 m depth the PDW was sampled which is characterized with a relatively high organic alpha of $10^{13.39}$.

In the region north of the SAF and PF at station 199, generally high organic alphas are found (higher than 10^{13}). In the surface layer of about 250 m, a wind mixed layer of at least 100 m is present from which the lowest sample (100 m) has a relatively low organic alpha of $10^{12.61}$. This is remarkable since the values of all other measured parameters in this wind mixed layer do not vary with depth (Fig. 2) except the organic ligand characteristics, the ligand concentration and the organic alpha (Table 2). Below 200 m, where the hydrography and the nutrient data indicate a different water type (Figs. 2 and 3), two organic ligands could be detected and the organic alpha is highest in these samples ($10^{13.7}$–$10^{13.9}$).

Hydrography appears to be the determining factor in the variation in the observed complexation characteristics.

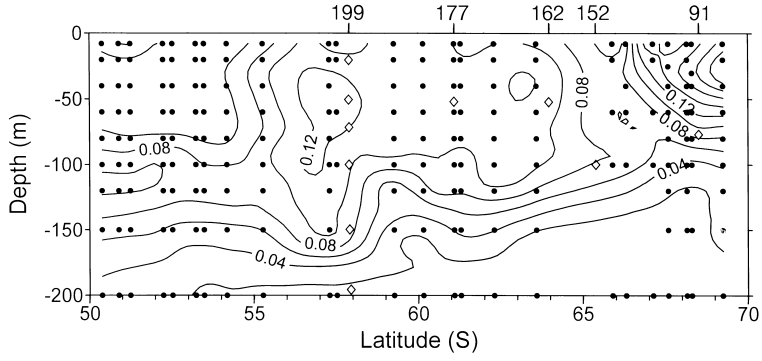


Fig. 7. Vertical section of the investigated area with contours of equal concentrations of chlorophyll *a* (mg/m^3) (courtesy of M. Templin and U. Bathmann, Alfred Wegener Institute, Germany). The data points for chlorophyll *a* are indicated by dots, the position of the samples in which speciation of Fe is measured are indicated by open diamonds. The stations numbers (this study) are given at the top of this figure.

By means of physical separation (de Baar et al., 1998) and chemical speciation (this work) various operationally defined forms of Fe are distinguished: dissolved organically complexed, dissolved inorganically complexed, colloidal or particulate. It is not known which of these species is most representative for biological uptake by phytoplankton and bacteria. Moreover, it is yet unclear by which mechanism algae can take up Fe (Wells et al., 1995). The mechanism of uptake may be very important in the discussion on bio-availability since the binding forces of organic and inorganic species of Fe are not very different, this in contrast with for example Cu (Sunda and Guillard, 1976). Thus the organic or inorganic nature of complexation may, or may not, be the discriminating factor in Fe bio-availability. At high organic percentage of total or dissolved Fe there are two possible mechanisms to ensure adequate Fe supply to (small) plankton cells: uptake of intact Fe-ligand complexes through the cell wall, or rapid kinetics of Fe-ligand dissociation in sea water with uptake of inorganic species. Either one of these mechanisms may be adequate for sustaining growth of small pico- and macro-plankton cells, the larger bloom-forming diatoms cannot flourish in these Fe-starved waters.

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